UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ODONTOLOGIA DE PIRACICABA

William Matthew Negreiros

Influência da aplicação de plasma de argônio não térmico nas propriedades mecânicas e transformação de fase da zircônia Y- TZP

Influence of non-thermal argon plasma on the mechanical properties and phase transformation of Y-TZP zirconia

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Dissertação apresentada à Faculdade de Odontologia de Piracicaba da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Mestre em Materiais Dentários.

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Orientador: Prof. Dr. Marcelo Giannini

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A Ata da defesa com as respectivas assinaturas dos membros encontra-se no processo de vida acadêmica do aluno.

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Resumo

O objetivo deste estudo foi avaliar a influência de diferentes tempos de aplicação de plasma de argônio frio (NTP) e do envelhecimento acelerado em autoclave na resistência flexural, módulo de elasticidade, conteúdo cristalino e caracterização da topografia de uma zircônia tetragonal policristalina (Y-TZP, ZirCAD, Ivoclar Vivadent). O NTP foi aplicado na zircônia por 0, 10 e 60 segundos. Para as análises da resistência flexural e módulo de elasticidade (teste de 4 pontos e velocidade de 1mm/min) foram preparados espécimes com dimensões de 45 mm de comprimento, 4.0 mm de largura e 3.0 mm de espessura (n = 10) e o envelhecimento artificial em autoclave realizado por 0 (*baseline*), 4 e 30 horas. Os dados foram analisados estatisticamente pela análise de variância 2 fatores e teste de Tukey (α=5%). Para caracterização do conteúdo cristalino (volume monoclínico) da zircônia em função do tempo de envelhecimento e tratamento com NTP, um espécime por grupo foi submetido à análise por difração de raios-x (XRD) nos tempos de envelhecimento de: 0, 2, 4, 6, 8, 10, 15, 20 e 30 horas. A análise topográfica do material foi realizada em microscopia de força atômica no modo "sem contato" utilizando os mesmos espécimes avaliados em XRD. Os resultados mostram que não houve interação entre tipo de tratamento e tempo de envelhecimento em autoclave para os resultados de deflexão e módulo ($p>0.05$). O tempo de 30 horas de envelhecimento em autoclave resultou em aumento estatisticamente significativo dos resultados de resistência flexural quando comparado ao *baseline* para o grupo controle ($p<0.05$). Com relação ao módulo de elasticidades o tempo de 30 horas de envelhecimento produziu aumento significativo quando comparado ao *baseline* e 4 horas para todos os tratamentos ($p<0.05$). O conteúdo monoclínico tendeu aumentar com o envelhecimento artificial da zircônia. Não foi observada nenhuma alteração nas superfícies da zircônia independente do tratamento e tempo de envelhecimento. A aplicação de NTP mostrou não afetar negativamente as propriedades mecânicas da Y-TZP testada. O volume monoclínico aumentou em função do tempo em autoclave, sendo levemente maior nos espécimes tratados com NTP. O envelhecimento modifica o arranjo cristalino da Y-TZP e juntamente com o NTP não alteraram a topografia de superfície da mesma.

Palavras chave: Zircônio, Resistência de Materiais, Módulo de Elasticidade, Transição de Fase, Envelhecimento, Plasma de Argônio

Abstract

The objective of this study was to evaluate the influence of different times of non-thermal plasma (NTP) application and the accelerated aging in autoclave on flexural strength, elastic modulus, crystalline content and topography characterization of an Yttrium-stabilized Tetragonal Zirconia Polycrystal (Y-TZP, ZirCAD, Ivoclar Vivadent). The NTP was applied onto the zirconia surface for 0, 10 and 60 seconds. For flexural strength and modulus (4-point bending test at a crosshead speed of 1 mm/min) specimens with dimensions of 45 mm in length, 4.0 mm in width and 3.0 mm in thickness were prepared (n=10) and the accelerated aging in autoclave was conducted for 0 (baseline), 4 and 30 hours. Data were analyzed by 2-way ANOVA and post-hoc Tukey test (α=5%). To analyze the crystalline content of the zirconia specimens (monoclinic volume) in function of NTP treatment and aging, one specimen from each group was submitted to X-Ray Diffraction (XRD) after the following aging periods: 0, 2, 4, 6, 8, 10, 15, 20 and 30 hours. Topographic analysis of the same specimens submitted to XRD was performed with atomic force microscopy (AFM) in "non-contact" mode. Results show no interaction between type of treatment and aging time in autoclave for flexural strength and modulus ($p>0.05$). At 30 hours of aging in autoclave, there was a statistically significant increase in the flexural strength when compared to baseline in the control group ($p<0.05$). At 30 hours of aging, elastic modulus showed a statistically significant increase when compared to baseline and 4 hours for all types of treatment ($p<0.05$). Monoclinic content tended to increase following the zirconia aging. No change in zirconia surfaces was observed regardless of treatment and aging time. NTP application did not negatively affect the mechanical properties of the tested Y-TZP. Monoclinic volume increased as a function of time in autoclave, being slightly higher in NTP treated specimens. Aging modifies the crystalline phase of Y-TZP and, along with NTP, it does not alter surface topography.

Keywords: Zirconium, Material Resistance, Elastic Modulus, Phase Transition, Aging, Argon Plasma

Sumário

1. INTRODUÇÃO

O dióxido de zircônio foi descrito pela primeira vez na ciência dos materiais em 1975 pelos autores Garvie e Nicholson (Garvie, Hannink, & Pascoe, 1975). O artigo intitulado de “Ceramic Steel” pela primeira vez sugeriu a possibilidade de utilizar o material para situações que demandavam alta resistência mecânica. Nesse estudo os autores descobriram a possibilidade de produzir um material parcialmente estabilizado composto por diferentes estruturas cristalinas com propriedades mecânicas superiores. O dióxido de zircônio (ZrO_2) foi estabilizado por óxido de magnésio, contudo, outros estudos mostraram a possibilidade de se utilizar outros óxidos metálicos como por exemplo o CeO_2, CaO e o Y_2O_3 que, ao longo dos anos, tornou-se o composto principal de cerâmicas de ZrO_2 por apresentar-se mais estável que outros óxidos metálicos estabilizadores (Chevalier, 2006; Lawson, 1995) e atualmente é descrita como “zircônia tetragonal policristalina estabilizada por ítrio” (Y-TZP). Dessa forma, o material passou a ser usado pela indústria como isolante térmico e elétrico, e também para aplicações biomédicas (Chevalier, 2006; Christel, 1989; Lughi & Sergo, 2010; Manicone, Rossi Iommetti, & Raffaelli, 2007). A primeira aplicação biomédica deste material foi na substituição de cabeças de fêmur em pacientes com necessidade de próteses ortopédicas (Chevalier, 2006; Christel, 1989). O uso da Y-TZP mostrava-se favorável em relação à alumina, que é considerado um material muito friável, e oferecia alto potencial de fratura dos implantes (Chevalier, 2006).

A Y-TZP possui três fases cristalinas distintas: 1) monoclínica (*m*) em temperatura ambiente até 1170ºC; 2) tetragonal (*t*) acima de 1170ºC até 2370ºC; 3) Cúbica (*c*) acima de 2370ºC (Kelly & Denry, 2008). A zircônia biomédica encontra-se em um estado tetragonal metaestável a temperatura ambiente graças a adição de óxido de ítrio (Lughi & Sergo, 2010). Um material em estado metaestável é todo material que associa uma restrição que previna a transição imediata de sua fase mais estável caso não ocorra distúrbios externos. Assim, no caso da Y-TZP, um distúrbio externo pode causar a mudança da fase tetragonal para a monoclínica ($t \rightarrow m$) que por sua vez é acompanhada por uma expansão de 4% em seu volume (Denry & Kelly, 2008; Hannink, Kelly, & Muddle, 2000). Por um lado, isso confere a Y-TZP alta tenacidade à fratura pois, esse aumento de volume é responsável pela constrição da extremidade da fratura e sua possível anulação por constrição (Hannink et al., 2000). Por essa razão a Y-TZP é tão resistente. Contudo, esse mesmo mecanismo pode ser desfavorável na presença de outros distúrbios, como por exemplo, a mudança de fase por contato com agua, que induz à transformação de t→m de forma induzida, podendo gerar resultados catastróficos (Borchers et al., 2010; Cattani-Lorente, Scherrer, Ammann, Jobin, & Wiskott, 2011; Kim, Han, Yang, Lee, & Kim, 2009). Esse foi o caso da empresa Prozyr cuja as próteses femorais, fraturaram em alta quantidade entre 2000 e 2002 (Chevalier, 2006). Teoriza-se que esse fenômeno físico ocorra pela dissociação de H_20 em O^{2-} na superfície do cristal e esse produto da dissociação ocupe o espaço de uma vacância de oxigênio presente dentro da estrutura cristalina do material que, por sua vez, contrai a estrutura molecular do cristal, gerando tensão e consequentemente, mudando de fase cristalina.

Na mesma época em que os ortopedistas notaram a deficiência do material, a comunidade odontológica começou a utiliza-lo de forma exponencial graças ao advento do CAD/CAM, que se tornou uma realidade para a prática clínica de muitos profissionais (Chevalier, 2006). Seu alto potencial estético e alta resistência mecânica, permitiu que dentistas indicassem o material para diversas situações clinicas aumentando seu uso significativamente (Alfawaz, 2016; Y. W. Chen, Moussi, Drury, & Wataha, 2016). As primeiras indicações eram limitadas a infraestruturas de próteses fixas dento suportadas e implanto suportadas. Atualmente, graças ao desenvolvimento do material, sua indicação passou ser também para coroas monolíticas e até mesmo implantes de corpo único (Y. W. Chen et al., 2016; Pieralli, Kohal, Jung, Vach, & Spies, 2016).

Uma desvantagem do material é o baixo potencial adesivo com relação ao cimento resinoso (Tzanakakis, Tzoutzas, & Koidis, 2016). Por ser uma estrutura policristalina sem a presença de matriz vítrea e silício em sua composição, o condicionamento ácido convencional com ácido hidrofluorídrico (HF) 10% e sua posterior sinalização são ineficientes (Borges, Sophr, de Goes, Sobrinho, & Chan, 2003). A Y-TZP só pode ser condicionada com HF a partir de 60% ou ácido sulfúrico o que torna o procedimento clinicamente inviável. O silano por sua vez tem a função de se ligar a moléculas contendo silício por ligações siloxano, que aumenta significativamente a resistência de união de cerâmicas vítreas aos cimentos resinosos. Contudo, a Y-TZP é composta de 95 – 99% de cristais de ZrO_2, que não torna possível a utilização de silanos. Devido a esses fatores, muitos estudos focaram em uma alternativa para a união adesiva da zircônia. Dentre eles, podem ser citados a abrasão a ar por jateamento com partículas de óxido de alumínio com ou sem revestimento de sílica e posteriormente a aplicação de *primer* com um grupo funcional fosfato (10-MDP) (Inokoshi, De Munck, Minakuchi, & Van Meerbeek, 2014). O jateamento promove a limpeza da superfície do material e a formação de micro rugosidades (Yang, Barloi, & Kern, 2010), que aumenta a energia de superfície da cerâmica e favorece o molhamento do *primer* sobre ela. Estudos *in vitro* e *in vivo* mostram que o 10-MDP possui potencial adesivo à zircônia pela reação do grupamento fosfato com os óxidos da zircônia (Inokoshi et al., 2014; Kern, 2015, 2016; Ozcan & Bernasconi, 2015). Em um estudo clinico de 5 anos, Sasse e colaboradores mostrou 100% de sobrevida de 30 próteses adesivas com infraestrutura em zircônia em laterais em *cantilever* (Sasse & Kern, 2013). Durante esse período, apenas uma prótese se soltou, mas foi passível de re-cimentação, justificando o achado de 100% de longevidade clinica no grupo avaliado (Sasse & Kern, 2013). Todavia, para que as próteses fossem corretamente cimentadas, os autores realizaram jateamento com partículas de oxido de alumínio e a subsequente aplicação de um *primer* contendo 10-MDP. O sucesso clínico das próteses durante o período de estudo pode estar relacionado a sua indicação, onde contatos oclusais em incisivos laterais superiores é muito baixo, podendo em algumas situações ser até nulo. Procedimentos que envolvam a utilização de abrasão com pontas diamantadas e/ou abrasão a ar em restaurações Y-TZP, promovem a transformação de t→m podendo alterar as propriedades mecânicas e até mesmo aumentar a sua susceptibilidade a degradação hidrolítica (LTD). Assim, é importante que novas tecnologias que possam substituir o tratamento convencional de jateamento com óxido de alumínio sejam desenvolvidas para que restaurações em regiões de alta carga oclusal atinjam alta longevidade clínica.

Entre as novas tecnologias, o plasma de argônio frio (NTP) pode ser uma alternativa para aumentar a resistência de união de um cimento resinoso a zircônia (M. Chen et al., 2013; Lopes., Ayres., Lopes., Negreiros., & Giannini., 2014; Valverde et al., 2013). Sua tecnologia baseia-se na emissão de plasma contento íons, elétrons e moléculas em uma natureza não balanceada, promovendo assim a alteração da molhabilidade da superfície tratada. Sua aplicação pode ser utilizada para a limpeza, condicionamento, funcionalização de superfície e deposição de filmes. Alguns autores mostraram resultados promissores na aplicação de NTP para aumentar a resistência de união à zircônia (Lopes. et al., 2014; Valverde et al., 2013), adesão celular a superfície de implantes e *abutments* (Annunziata et al., 2016; Canullo, Genova, et al., 2016; Garcia et al., 2016), limpeza de superfície e esterilização (Annunziata et al., 2016; Canullo, Tallarico, et al., 2016). Sugere-se que a aplicação de NTP não promova alterações nas propriedades físico-mecânicas e químicas do material, dessa forma sendo indicada para a aplicação na zircônia.

Contudo, não se sabe se a aplicação de NTP pode acelerar a t→m, especialmente quando em contato com a água.

Diante do exposto, e das incertezas em relação a aplicação de novas tecnologias que visam a melhora da propriedade adesiva no processo de cimentação de peças protéticas de Y-TZP, o objetivo geral do presente estudo foi avaliar a influência da aplicação de NTP nas propriedades físicas de uma zircônia Y-TZP comercial.

Os objetivos específicos desse estudo *in vitro* foram:

- Analisar a resistência flexural e módulo de elasticidade do material após a aplicação de plasma e seu posterior envelhecimento em autoclave por até 30 horas;
- Avaliar a influência da aplicação de plasma na transformação de fase da zircônia e após envelhecimento em autoclave por até 30 horas.
- Caracterizar a superfície da zircônia em microscopia de força atômica (AFM);

2. ARTIGO

Influence of non-thermal argon plasma on the mechanical properties and phase transformation of Y-TZP zirconia.

Artigo submetido ao periódico (Anexo 1) “Journal of Prosthetic Dentistry”

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2.1Abstract

Statement of problem: Low temperature degradation (LTD) is the one of major concern regarding zirconia ceramics. Moreover, because the indication to treat zirconia surface for bonding with plasma, the long-term effect of non-thermal plasma (NTP) on the acceleration of LTD on zirconia surfaces has not being described.

Purpose: The aim of this study is to evaluate the mechanical properties of a commercial Y-TZP by means of flexural strength test and modulus, as well as assess changes in crystalline phase transformation and surface topography after application of NTP, during different aging periods.

Material and Methods: For flexural strength and modulus test, ninety Y-TZP (45 mm length x 4 mm width x 3 mm thick) bars were randomly assigned to the following groups (n=10): NTNA: no treatment/baseline; NT4A: no treatment + 4 hours aging; NT30A: no treatment + 30 hours aging; 10NTPNA: 10 seconds of NTP/baseline; 10NTP4A: 10 seconds of NTP + 4 hours aging; 10NTP30A: 10 seconds of NTP + 30 hours aging; 60NTPNA: 1 minute of NTP/baseline; 60NTP4A: 1 minute NTP + 4 hours aging; 60NTP30A: 1 minute NTP + 30 hours aging. Flexural strength and modulus was assessed with a universal testing machine at a crosshead speed of 1 mm/minute until failure. Data were analyzed by two-way ANOVA and post hoc Tukey tests ($\alpha<0.05$). Accelerated aging was simulated in an autoclave at 134ºC, under a pressure of 2 bar for up to 30 hours. Monoclinic volume was evaluated by using X-Ray Diffraction (XRD) in different periods (0, 2, 4, 6, 8, 10, 15, 20 and 30 hours) utilizing a specimen from the groups NT30A, 10NTP30A and 60NTP30A. Surface topography was assessed by means of atomic force microscopy (AFM) during different periods (baseline, 4, and 30 hours) with the same specimens analyzed for XRD.

Results: For both the flexural strength and modulus, there was no significant difference when comparing different treatments to zirconia. There was no interaction among treatments and aging time. A significant increase in flexural strength after 30 hours of aging for the control group was obtained when compared to baseline value. Regarding modulus, a significant increase was found after 30 hours of aging in all groups when compared to baseline and 4 hours. Monoclinic

volume tended to increase as function of time in all groups, showing to be slightly higher for groups treated with NTP. No difference in surface topography was observed among treatments nor aging.

Conclusions: LTD of tested zirconia showed an increase in flexural strength for the control group after 30 hours. For modulus, an increase was observer for all groups after 30 hours. Aging increased m-phase volume in all specimens. Surface topography was not influence by LTD regardless of time and treatment.

Clinical Implications: Clinicians may consider the use of NTP on treating zirconia surfaces for bonding without affecting mechanical properties. The present study may encourage the use of different non-damaging surface treatment protocols for zirconia luting.

2.2 Introduction

The introduction of the toughening mechanism of zirconia ceramics in the mid-1970s contributed to extensive research on its biomedical applicability. [1-19] In the early 2000s, yttrium-tetragonal poly-crystal zirconia (Y-TZP) became an alternative to porcelain fused-to-metal restorations and frameworks and it is possibly the most common type of zirconia used in general practice today. [6] Providing good biocompatibility, superior esthetics and favorable mechanical properties, its applicability ranges from copings, abutments, monolithic crowns, fixed partial dentures (FPDs) and even dental implants made of zirconium dioxide. [19-21] Moreover, the production of such restorations became easier since the development of chair-side CAD/CAM systems, enabling clinicians to deliver faster treatments with better quality.

Zirconia is known to assume three crystallographic forms depending on temperature. At room temperature until 1170^{o}C it is monoclinic (m). Above that and up to 2370^{o}C, it becomes tetragonal (t). Finally, when it reaches higher than 2370^{o}C, it is cubic (c). [10-12,14,22] During cooling, at around 950^{o}C, t→m transformation occurs and it is accompanied by a volumetric increase of approximately 4.5%, leading to catastrophic failures due cracking. To prevent such an event, alloying zirconia with metal oxides (eg. Y_2O_3) became an alternative to maintain the tetragonal phase at a metastable state at room temperature, therefore t→m transformation is hindered.

It is well established in the scientific community that to achieve durable bond to resin cements, zirconia ceramics must undergo surface treatments such as grinding and sandblasting. [13, 15, 16, 23-25] Another trend is to diminish the use of metal alloy materials like titanium implants, for esthetic reasons. Patients who possess thin gingival biotype may not fulfill their esthetic expectations, thus zirconia implants might be required to prevent possible drawbacks. Furthermore, it is well-documented that a rough surface is favorable for osseointegration and endosseous anchorage. [26] Several strategies are used to create roughness on implants (acid etching, sandblasting, surface coating). [27] However, due the meta-stability of the material, any stress-inducing treatment that has the potential to damage its surface, promotes t→m transformation. In one hand, this increases mechanical properties like flexural strength due to compressive stresses, on the other hand however, altering phase integrity may increase the material susceptibility to aging specially for porous surfaces. [28] This phenomenon is known as “Low Temperature Degradation” (LTD) and is characterized by the progressive t→m transformation under wet environment. [29-32] As consequences of such problem it has been reported volumetric changes, micro crack formation, grain pullout, surface roughening and, as result, mechanical degradation. [6, 29, 33, 34] To avoid accelerate aging, a viable option is to alter the surface chemistry with procedures that are not stress-inducing.

Among new treatments available, non-thermal plasma (NTP) for surface modification shows promising results. NTP discharges have been widely used with great success in the industrial field. [35] Its applications on surface modification techniques range from etching, cleaning, plasma radiation for decontamination of surfaces, functionalization and deposition of films onto the surface of bulk materials. [35, 36] NTP application is a potential mechanism to enhance resin bond strength to zirconia and cell adhesion to titanium and zirconia implants. [37-42] It works by altering surface chemistry and increasing surface energy without the possible deleterious effects of stress inducing treatments. [35-37,43] The success of this technology relies on its non-equilibrium nature, which has the potential to react with numerous surfaces by providing high doses of chemically active species at low temperature. [35-37,44] Thus, modifying and increasing reactivity of surfaces without damaging the bulk properties of the material. [19]

Because the interaction of NTP on zirconia based materials has not been thoroughly researched, this investigation tested the following null hypothesis: (1) NTP and hydrothermal aging would not negatively affect the zirconia flexural strength or modulus and (2) NTP would not accelerate t→m transformation; (3) Hydrothermal aging would not influence t→m transformation (4) NTP and autoclave aging would not change the zirconia topography.

2.3 Materials and methods

For this research, one type of yttrium stabilized zirconia polycrystal (Y-TZP) dental ceramic block (ZirCAD, Ivoclar Vivadent) was used to investigate the effect of NTP. Ninety bar-shaped specimens were cut with a precision cutter (Isomet 1000, Buehler) in predetermined dimensions to compensate sintering shrinkage and meet ISO 13356 standards. Specimens were sintered at 1450^{o}C for 1 hour to prevent an increase in cubic content. [22] Subsequently, they were polished with 250, 600 and 1200 grit diamond discs, and by cloth discs combined with 3 μm and 1 μm diamond polishing pastes.

Later, thermal annealing was performed for 20 minutes at 1350^{o}C to expose grain boundaries and to ensure only the formation of tetragonal grains. Specimens were randomly assigned into the following groups (n = 10):

Group NTNA: No NTP treatment / no aging
Group NT4A: No NTP treatment / 4 hours aging
Group NT30A: No NTP treatment / 30 hours aging
Group 10NTPNA: 10 seconds of NTP / no aging
Group 10NTP4A: 10 seconds of NTP / 4 hours aging
Group 10NTP30A: 10 seconds of NTP / 30 hours aging
Group 60NTPNA: 60 seconds of NTP / no aging
Group 60NTP4A: 60 seconds of NTP / 4 hours aging
Group 60NTP30A: 60 seconds of NTP / 30 hours aging

The NTP equipment used in the study (Surface – Engineering and Plasma Solution Ltda) consists of a hand-held unit (130 mm length x 30 mm diameter), with a quartz nozzle (4 mm length x 2 mm diameter) attached to a high voltage power supply used to produce a non-thermal plasma torch at atmospheric pressure. High purity Argon (Praxair 4.8, White Martins Gases) with an output of 5 liters per minute was used to produce a plasma plume. The torch exiting the nozzle was 20 mm long x 2 mm diameter and was operated at room temperature of 22^{o}C. Distance between the nozzle and the treated surfaces was 10 mm, and when plasma was used, the exposure time was 10 and 60 seconds. The hand-held unit was placed vertically to the exposed surfaces and homogeneously applied onto the entire specimen.

The artificial accelerated aging of zirconia specimens was performed in autoclave (Vitale Plus, Cristófoli) for 0 (or baseline), 4, and 30 hours (in water steam at 134°C, under two bar pressure). These accelerated aging times were selected, because some authors have hypothesized that one hour in an autoclave cycle at 134°C represents approximately 2-3 years at 37°C in vivo. [6-8, 27]

To determine flexural strength and modulus before and after aging of groups, specimens underwent four-point bending test as described by ISO 13356. Strength was measured by using 4-point (20 x 40 mm) spans. Specimens with dimensions of 45 mm in length, 4.0 +/- 0.2 in width and 3.0 +/- 0.2 in thickness were tested.

Testing was conducted at ambient temperature, with an universal testing machine (4411, Instron), at a crosshead speed of 1 mm/minute to avoid slow crack growth before failure. Collected data comprise of maximum load until failure and modulus of both aged and control group. Flexural strength (MPa) and modulus (GPa) data were obtained with Bluehill2 software (Bluehill2, Instron) and analyzed by two-way ANOVA (“Aging” and “Treatment”) and post-hoc Tukey test ($\alpha = 5$).

A specimen from groups “NT30A”, “10NTP30A”, “60NTP30A” were subjected to XRD analysis for different periods (0, 2, 4, 6, 8, 10, 15, 20, 30 hours) so that monoclinic volume change was investigated. Monoclinic content on treated surfaces was assessed by means of X-ray diffraction (XRD) with CuKα radiation (40 kV, 40 mA). Scans were performed with an angulation range of 27-33 degrees (2Θ) at a scan speed of 0.2 degrees/minute with a step size of 0.02 degrees.

Monoclinic phase fraction (Xm) was measured with Garvie and Nicholson formula [45]:

$$X_m = \frac{I_{m(\bar{1}\ 1\ 1)} + I_{m(1\ 1\ 1)}}{I_{m(\bar{1}\ 1\ 1)} + I_{m(1\ 1\ 1)} + I_{t(1\ 0\ 1)}}$$

Where *It* and *Im* represent the integrated intensity (area under peaks) of the tetragonal (101) and monoclinic (111) and (-111) peaks. Monoclinic volume content was calculated as described by Toraya et al. [46]

$$V_m = \frac{1.311X_m}{1 + 0.311X_m}.$$

The same specimens used in XRD analysis were investigated to evaluate changes in surface topography by means of atomic force microscopy (AFM). AFM (EasyScan2 FlexAFM Nanosurf, NanoScience Instruments) analysis was conducted in non-contact mode, with a highly silicon doped probe with tip radius of less than 8 nm.

2.4 Results

Flexural strength and modulus for experimental groups are described in Tables 1 and 2. Two-way ANOVA and Tukey test demonstrated that NTP did not influence the flexural strength and modulus following aging times (0, 4, and 30 hours). For group NT30A (no NTP application), the aging time for 30 hours significantly increased the flexural strength compared to the baseline ($p < 0.05$). For flexural modulus, there was significant increase for all groups (NT30A, 10NTP30A 60NTP30A) after 30 hours of aging in autoclave, compared to baseline and four hours of autoclave aging ($p < 0.05$). No interaction between "Aging" and "Treatment" was found ($p > 0.05$) neither for flexural strength and modulus.

XRD analysis (Figure 1) shows no presence of m-phase during baseline (no NTP and no aging). For groups with four and thirty hours of aging it is noticeable an intensity increase in -111 and 111 peaks, indicating that t→m resulted from the autoclave cycle. Monoclinic volume (Table 3) showed that all groups presented t→m transformation after aging and seemed that the increase was higher for the groups treated with NTP. No significant alterations were observed in zirconia topography, regardless of NTP treatment and aging time, according to the atomic force microscopy analysis (Figure 2).

2.5 Discussion

Aging significantly increased flexural strength and modulus of the zirconia tested, thus the first null hypothesis stating that NTP and aging would not negatively influence flexural strength and modulus should be partially accepted, because NTP did not decrease its mechanical properties. When flexural strength and modulus was analyzed, an increase in both values after 30 hours of accelerated aging was observed however, flexural strength statistically increased only for group NT30A (555.5 MPa). The increase in both tests could be explained by the higher m-phase content present in the material surface (Table 3), suggesting that t→m promotes compressive pressure on crack vicinities, consequently increasing mechanical properties of tested specimens. [12] Other studies also showed an increase in the mechanical properties values for Y-TZP zirconia ceramics after autoclave aging, which contained less than 50% of m-phase volume. [33, 34] Furthermore, the low content of m-phase value after 30 hours of aging (22.3% for NT30A, 30.8% for 10NTP30A, and 30.3% 60NTP30A) is directly related to the specimen roughness, being the most important parameter the material density. It is well established in the literature that porous ZrO_2 surfaces are more susceptible to LTD. [30] Because ISO 13356 instructions were followed, specimens were mirror polished. Moreover, according to the International Standard, specimens should contain less than 20% of m-phase to be clinically accepted. In the present study, this value was achieved only after 15 hours of autoclave aging for all groups (20.8% for NT30A, 21.5% for 10NTP30A, and 21.7% for 60NTP30A) suggesting high resistance to LTD. For more porous materials, such as implant surfaces that present lower density, water could easily permeate through the porosities and accelerate t→m transformation, which might affect mechanical properties negatively. Therefore, further studies must be conducted to assess the possible effects of NTP application to porous zirconia surfaces and its influence in LTD.

NTP application and aging influenced t→m transformation. In experimental groups m-phase value seemed to be higher when NTP and aging were concomitantly employed (Table 3). Thus, the second and third hypothesis stating that NTP and autoclave aging would not accelerate t→m transformation and would not influence aging must be rejected. After years of research many theories to explain the exact LTD mechanism of Y-TZP zirconia have been suggested. [3-8, 10, 11, 14, 17-19, 22, 27, 30-32, 34] The accepted theory is that moisture (H_2O) when in contact with the ZrO_2 ceramic reacts with O_{2-} forming hydroxyl groups (OH^-). Later, these hydroxyl groups permeate within grain boundaries binding to oxygen vacancies present in the Y-TZP zirconia thus forming proton structural defects. Finally, the tetragonal phase is no longer stable. [11] The t→m transformation is a “martensitic transformation”, where there is a change in structural coordination and change in structure of crystals without atom diffusion.

It is common to find suggestions for zirconia bonding in the literature. [13, 15, 24, 25] However, most studies have reported difficulties to maintain durable bond strength after storage. [13, 15, 24] NTP discharge has the potential to improve bonding without damaging the surface and become an alternative for more aggressive procedures (e.g. air-particle abrasion). [37] The effect of

NTP on t→ m was measured by accelerate artificial aging tests. A study suggested that one-hour of autoclave aging at 134ºC and two bar pressure, represents 2-3 years in vivo. [7] Because it would be a strenuous task to conduct a study to analyze t→m transformation at 37ºC in moist environment, frequently researchers use this methodology. [4, 6, 7, 18, 27, 30, 34] To verify the possible influence NTP has on Y-TZP zirconia, this study aged the specimens immediately after treating its surfaces. Authors have suggested that the hydrophilic potential of NTP lasts for a short period; therefore, they had to be aged as fast as possible. [43] Phase volume analysis shows that treated surfaces induced an accentuated t-m transformation (Table 3). One can suggest that by enhancing hydrophilicity, a Y-TZP zirconia becomes vulnerable to water absorbance, hence increasing the rate of t→m transformation by dissociation of O_2^-. Moreover, NTP discharges are rich in hydroxyl groups [35, 36] and can strongly influence the concentration of oxygen on the Y-TZP zirconia surface [37] thereupon, accelerating the rate, which hydroxyl groups fill the ZrO_2 crystal vacancies. However, further studies must be conducted to elucidate how this mechanism ought to work.

One could suggest that NTP application itself could lead to t→m; however, XRD analysis showed no indication of m-phase peaks (111 and -111) before aging took place (Figure 1). To analyze the effect of the NTP on the zirconia surface, immediately after AFM and XRD analysis, specimens were subjected to autoclave aging. The surfaces treated with NTP are reactive for up to five hours; [43] therefore, the time necessary to analyze its crystallographic phase and topography were below this period. Although this in vitro study showed the possible influence of accelerated aging on a surface treated with NTP, in a clinical case scenario the effect of NTP would cease in around five hours, which means that aging would no longer be influenced after this time. Because one hour of autoclave aging corresponds to two-three years in vivo, one could suggest that the potential damage withstood by treated specimens would not be correlated to that of exposed zirconia to the oral environment. However, studies like the present one are necessary to elucidate questions about novel treatments and technologies before they are put to practice in vivo, thus avoiding disastrous episodes as those perceived in a medical prosthesis company where the lack of laboratorial investigation led to catastrophic failures in 2001.[6]

Studies have shown that autoclave aging of zirconia specimens is responsible for t→m transformation. In the present study, specimens were submitted to a variety of aging periods. It is possible to conclude that exposing zirconia to autoclave aging can significantly influence the final m-phase volume. This finding corroborates with other investigations showing similar results. [3-8, 10, 11, 22, 23, 30, 33]

Aside from increasing surface reactivity, in some cases, NTP is used for various surface treatments (e.g. etching). [35] AFM produced images showing similar topography among groups, regardless of treatment and aging time. Thus, the fourth hypothesis stating the NTP and autoclave aging would not change the zirconia topography was accepted. These results corroborate with an investigation, who also found little difference in surface topography. [23] Other study demonstrated that autoclave-aging influenced surface topography, increasing the roughness by nucleation of crystals. [8] However, these studies analyzed surfaces that were both sandblasted and ground. It is clear in the literature that ground surfaces tend to be affected more by LTD and to form an irregular surface after aging due to nucleation. [6, 7, 8]

2.6 Conclusions

The results suggested that:

1- NTP showed not to be detrimental to the mechanical properties of the tested Y-TZP zirconia ceramic.
2- LTD in autoclave for 30 hours increased the m-phase content of the zirconia in all groups tested.
3- Surface topography of zirconia was not affected by NTP application regardless of time, aging and their combination.

Table 1. Flexural strength (MPa) of Y-TZP zirconia ceramic according to treatment and autoclave aging.

Treatment	Autoclave Aging (Time)		
	0 hours (baseline)	4 hours	30 hours
Control	358.2 (49.9) B a	495.4 (154.7) AB a	555.5 (187.8) A a
10s NTP	401.6 (98.0) A a	411.6 (175.2) A a	487.8 (147.7) A a
60s NTP	483.1 (115.2) A a	392.5 (120.4) A a	556.6 (213.4) A a

Upper case letter compare aging times within the same treatment (row) and lower case letters compare treatments within the same aging time (column).

NTP: Non-thermal Plasma

Table 2. Modulus (in GPa) of Y-TZP zirconia ceramic according to treatment and autoclave aging.

Treatment	Autoclave Aging (Time)		
	0 hours (baseline)	4 hours	30 hours
Control	179.5 (23.0) B a	165.3 (25.9) B a	236.0 (28.1) A a
10s NTP	169.8 (17.4) B a	163.9 (20.5) B a	237.4 (25.7) A a
60s NTP	170,0 (17.7) B a	171.4 (27.5) B a	236.6 (24.7) A a

Upper case letter compare aging times within the same treatment (row) and lower case letters compare treatments within the same aging time (column).

NTP: Non-thermal plasma.

Table 3. m-phase volume (%) analysis of all groups.

Aging (hours)	Groups		
	No / Treatment	**NTP 10 s**	**NTP 60s**
0 (baseline)	4.4	0.2	5.4
2	6.0	8.4	9.3
4	8,3	11.5	11.1
6	10.2	14.2	12.9
8	12,1	16.2	15.0
10	15.1	17.8	15.3
15	20.8	21.5	21.7
20	20.6	25.0	25.1
30	22.3	30.8	30.3

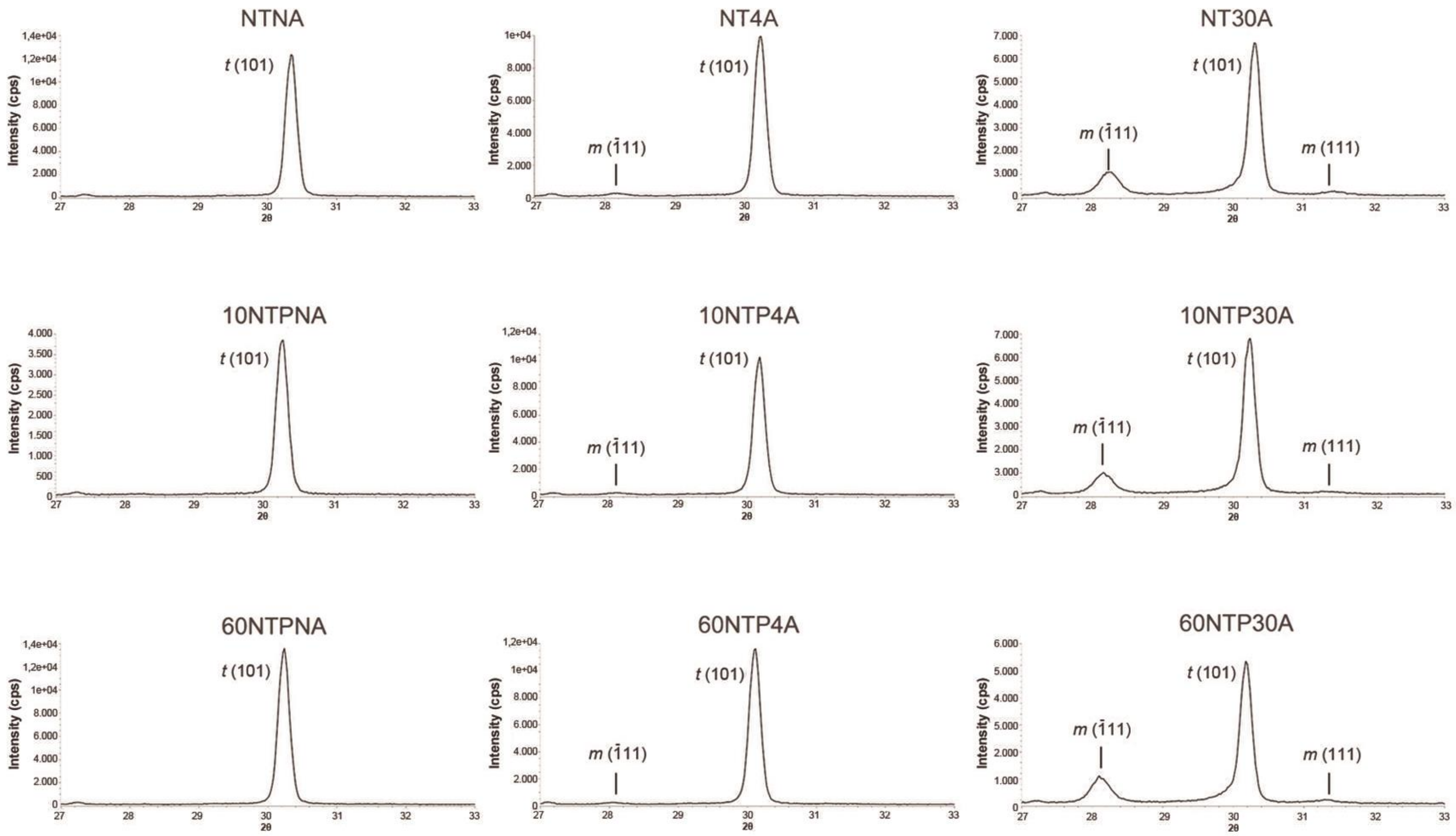

Fig. 1 – XRD patterns of different treatments and aging of zirconia specimens. (*m*) Monoclinic; (*t*) Tetragonal.

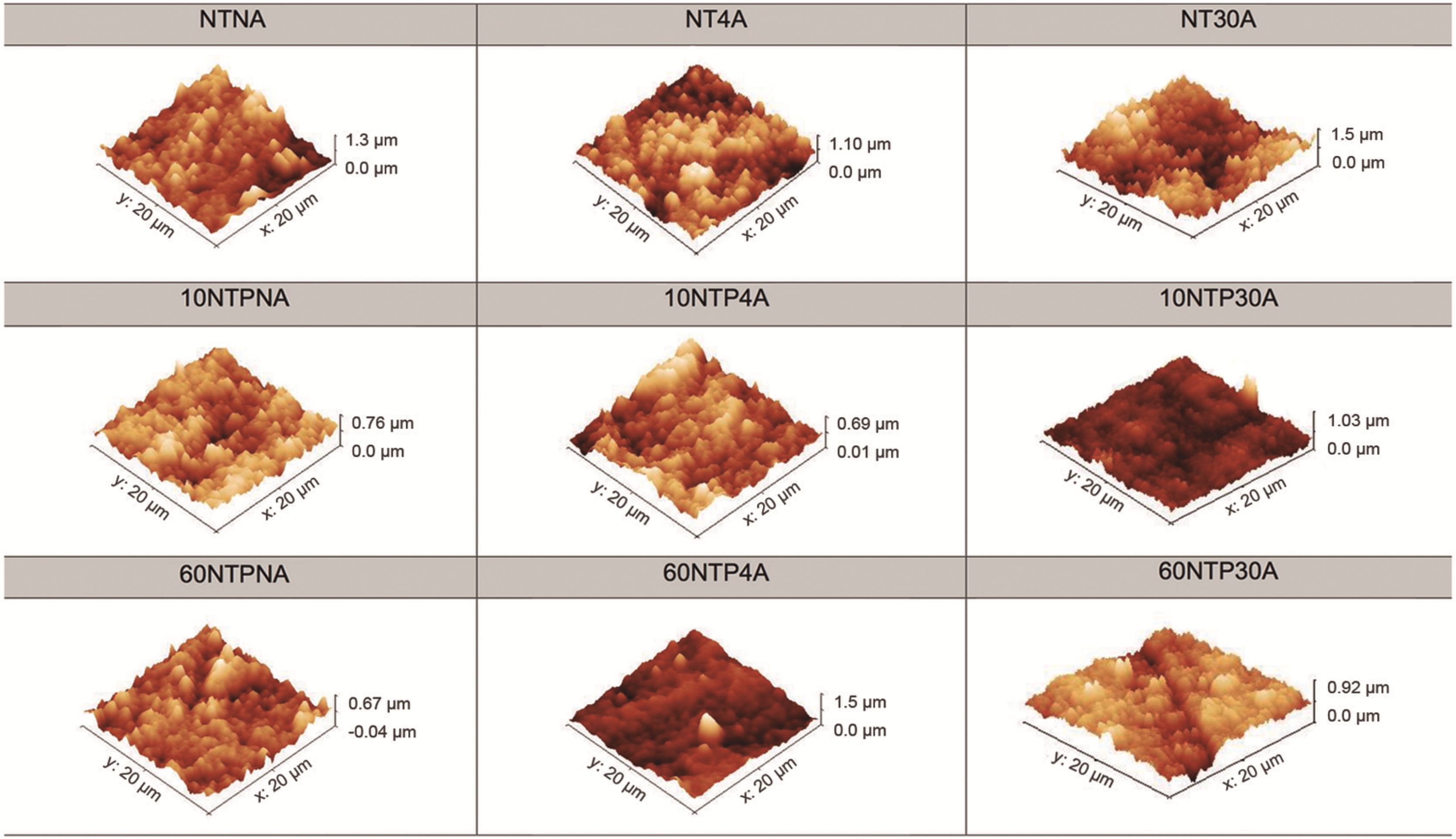

Figure 2. AFM images (20 µm × 20 µm) of experimental groups.

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3. CONCLUSÃO

A partir dos resultados obtidos no presente estudo, é possível concluir que:

- A aplicação de NTP não afetou a resistência flexural e o módulo de elasticidade, podendo assim ser utilizado em procedimentos adesivos de cerâmicas a base de zircônia;
- O envelhecimento em autoclave induziu a transformação de fase da zircônia de t→m e pode-se sugerir que o NTP talvez acentue a mesma. Porém, há a necessidade de estudos *in vivo* para que possa analisar a real influência do NTP no material quando em contato com umidade;
- Não foi encontrado diferença na topografia de superfície qualquer que fosse o tempo de envelhecimento do material, aplicação de NTP e nem a combinação deles.

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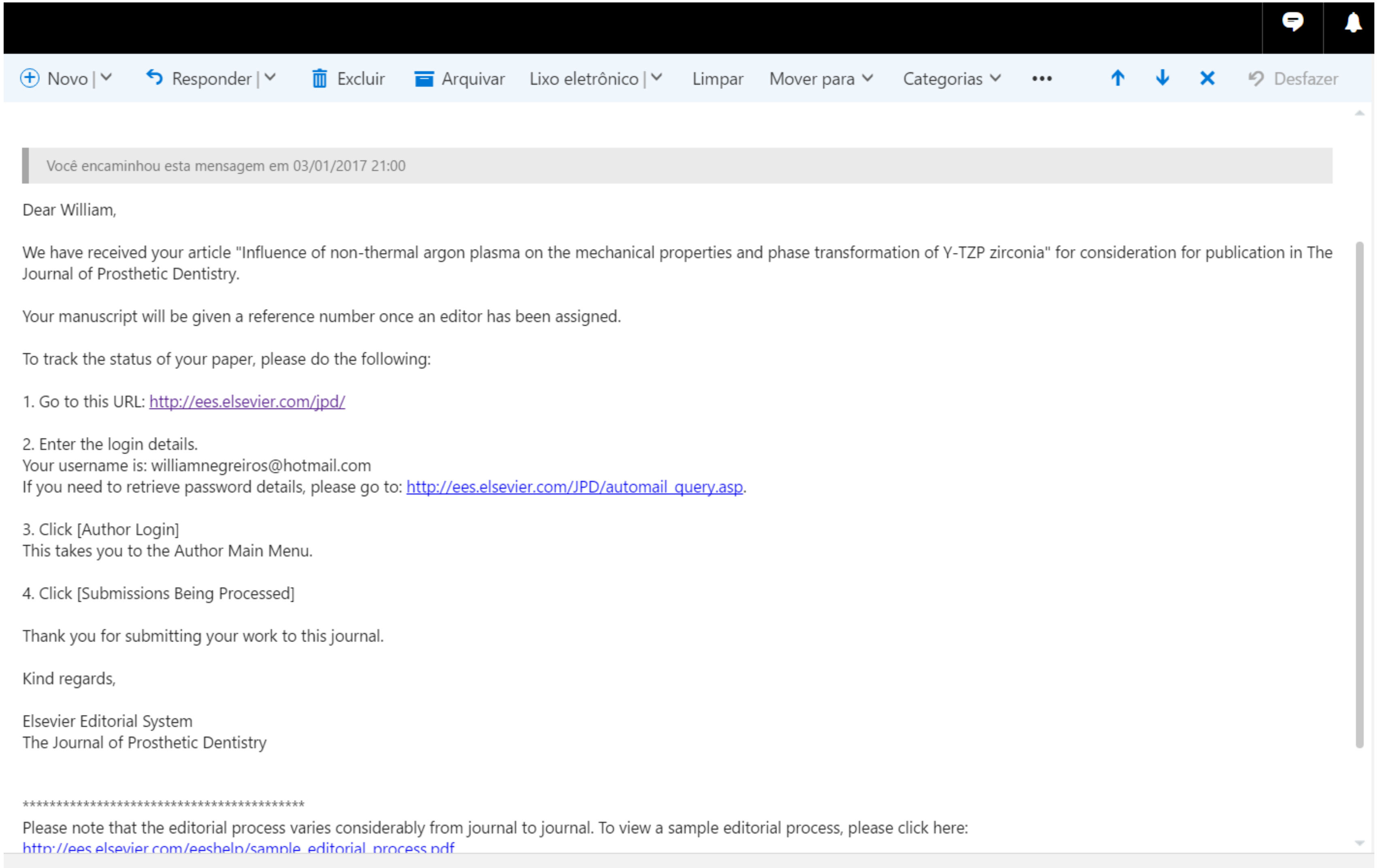
ANEXO 1



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